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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



In re application of  
KASZTELAN et al.

Serial No.: 09/603,838

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Examiner: Christina ILDEBRANDO,  
Group Art Unit: 1754

For : CATALYST THAT CONTAINS A ZEOLITE THAT IS HIGH IN AN ELEMENT OF GROUPS VIB AND/OR VIII AND ITS USE IN HYDROREFINING AND HYDROCRACKING OF HYDROCARBONS FRACTIONS.

**DECLARATION UNDER RULE 37 C.F.R. §1.132**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

I, Slavik KASZTELAN, being duly warned, declare and say as follows:

THAT, I am a French citizen ; that I obtained an Engineer Diploma delivered by "Ecole des Hautes Etudes Industrielles de Lille" (France) in 1982 ; that I was received as a "Docteur Ingénieur" in 1984 and as a "Doctor habilité à diriger des recherches" in 1991 by "Université de Lille" ; and that I know reside in 92500 Rueil-Malmaison, France, 27 Rue Raymond Queneau.

THAT, I was engaged on research by "Institut Français du Pétrole" Rueil-Malmaison (France) in their Kinetics and Catalysis Department in 1988, where I was continuously and actively in charge of researches in the fields of hydrocracking, hydroisomerization, dewaxing and hydrogenation of aromatic compounds; that from January 1995 to March 2001, I was Project Manager in the fields of "fundamental research in heterogeneous catalysis" and then of "hydrotreatment catalysts" ; and that since then I have been Manager of the Kinetics and Catalysis Research Division.

THAT, I am familiar with the processes and catalysts for hydrocracking.

THAT, I have supervised the following examples :

**Example 7: Production of Catalysts E and F not in Accordance to Procedure**

Catalysts E and F are prepared by comulling a Y zeolite with a molybdenum component and an alumina hydrogel in the following way : in a first step, a Y zeolite powder with a crystalline parameter that is equal to 2.429 nm and an overall Si/Al atomic ratio of 13.6 and an Si/Al framework atomic ratio of 19 is prepared, that is comulled with molybdenum oxide so as to mix 2.4% by weight of MoO<sub>3</sub> relative to the zeolite. This comulling method with molybdenum oxide enables to deposit the molybdenum on the exterior surface of the zeolite.

To obtain catalyst E, 20% by weight of the zeolite that is comulled with molybdenum oxide that is prepared above is used, that is mixed with 80% by weight of SB3-type alumina provided by the Condéa Compagny. The mixed paste is then extruded through a die with a 1.4 mm diameter. The extrudates are then dried for one night at 120°C under air and then calcined at 550°C under air. The extrudates are impregnated in the dry state, i.e., by filling the pore volume by an aqueous solution of a mixture of ammonium heptamolybdate, nickel nitrate and orthophosphoric acid, dried for one night at 120°C under air and finally calcined under air at 550°C. The composition of the impregnation solution is calculated to obtain on the final catalyst 2.2 % by weight of nickel oxide NiO, 12.3% by weight of molybdenum oxide MoO<sub>3</sub>, and 4.4% by weight of phosphorus oxide P<sub>2</sub>O<sub>5</sub>. The catalyst also contains 15.9% by weight of a Y zeolite.

To obtain catalyst F, 70% by weight of the zeolite that is comulled with molybdenum oxide that is prepared above is used, that is mixed with 30% by weight of SB3-type alumina provided by the Condéa Compagny. The mixed paste is then extruded through a die with a 1.4 mm diameter. The extrudates are then dried for one night at 120°C under air and then calcined at 550°C under air. The extrudates are impregnated in the dry state, i.e., by filling the pore volume by an aqueous solution of a mixture of ammonium heptamolybdate, nickel nitrate and orthophosphoric acid so as to deposit 1.5% by weight of nickel oxide NiO, 5.8% by weight of molybdenum oxide MoO<sub>3</sub>, and 2.5% by weight of phosphorus oxide P<sub>2</sub>O<sub>5</sub>. It is dried for one night at 120°C under air, and finally it is calcined under air at 550°C. In view of the initial presence of molybdenum on the zeolite, the catalyst contains by weight of oxide: 1.5% by weight of nickel oxide NiO, 7.3% by weight of

molybdenum oxide  $\text{MoO}_3$ , and 2.5% by weight of phosphorus oxide  $\text{P}_2\text{O}_5$ . The final catalyst contains 61% by weight of the Y zeolite.

**Example 8: Comparison of Catalysts C, D, E and F for Hydrocracking of a Vacuum Distillate with Moderate Pressure.**

The Catalysts E and F whose preparations are described in the example 7 are tested under the conditions of hydrocracking at moderate pressure as described in the example 5 with the same petroleum feedstock. The characteristics of catalysts E and F, their activity, gross conversion CB at  $400^\circ\text{C}$ , coarse selectivity SB, hydrodesulfurization conversion HDS and hydrodenitrating conversion HDN are compared in the following table with those obtained for catalysts C and D.

	C	D	E	F
Zeolite (%)	16.2	60.4	16.2	61
NiO (%)	2.2	1.5	2.20	1.5
$\text{MoO}_3$ (%)on alumina	12.3	7.3	12.3	7.3
$\text{P}_2\text{O}_5$ (%)	4.4	2.5	4.4	2.5
$\text{MoO}_3$ in or on zeolite (%) by weight of zeolite)	2.4	2.4	2.4	2.4
CB (% by weight)	49.3	56.9	48.8	55.2
SB	82.0	79.9	81	74.5
HDS (%)	99.6	99.7	99.6	99.6
HDN (%)	97.8	98.9	97.5	89.6

For a same amount of zeolite, oxide matrix, hydrogenating element and phosphorous, it is observed that catalysts containing molybdenum on the exterior surface of the zeolite (catalysts E and F) provide worse conversion levels of fraction  $380^\circ\text{C}^{\text{plus}}$  and worse selectivities than catalysts that contain molybdenum in the porous network of the zeolite (catalysts C and D). Furthermore, the presence of molybdenum in the porous network of the zeolite enables to improve the performances in hydrotreatment (hydrodesulfurization and hydrodenitrating).

The improvement of the conversion, the selectivity and the HDS and HDN activities due to the presence of molybdenum in the porous network of the zeolite is more marked when catalyst contains a large amount of zeolite.

**Example 9: Comparison of Catalysts C, D, E and F for Hydrocracking of a Vacuum Distillate with Higher Pressure.**

The Catalysts E and F whose preparations are described in example 7 are tested under the conditions of hydrocracking at high pressure as described in example 6 with the same petroleum feedstock.

In the following table, the reaction temperature for 70% gross conversion and the coarse selectivity for catalysts E and F are compared with those obtained for catalysts C and D.

	T (°C) for 70% Gross Conversion	SB
C	384	67
D	365	64
E	387	67
F	368	44

The comparison of catalysts C with D and E with F shows that by increasing the amount of zeolite, the activity of the catalyst that is indicated by the temperature level required to obtain 70% of conversion of the feedstock is considerably increased. In the case where molybdenum is deposited on the exterior surface of the zeolite, this increase of activity leads to a significant loss of selectivity. In the case where molybdenum is deposited in the porous network of zeolite, the level of selectivity is maintained when the amount zeolite increase.

In short, catalysts containing molybdenum on the exterior surface of the zeolite are less active and less selective than catalysts that contain molybdenum in the porous network of the zeolite.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information or belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Rueil-Malmaison, June 21, 2002

A handwritten signature in black ink, appearing to read "Slavik KASZTELAN". The signature is fluid and cursive, with the name written in a stylized manner.

Slavik KASZTELAN